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Modeling K+ and Ag+ complexation by thiacalix[4]arene amides using DFT: The role of intramolecular hydrogen bonding

Shamova L., Shamov G., Antipin I., Konovalov A.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

Complexation of methyl-glycine-amide functionalized thiacalix[4]arene with K+ and Ag+ has been studied using density functional theory (DFT) in the gas phase. To account for the conformational possibilities of the ligand, the free ligand and its potassium complexes were subjected to global minima searches on the molecular mechanics (MM) level of theory with the OPLS (optimized potentials for liquid simulations) force field. For the free ligand, the order of the energies and geometries of the ligand conformers is in agreement between MM and DFT; however, the position of K+ in the ligand's cavity was predicted differently by these methods. Hydrogen bonding of amide hydrogens in the ligands' podand arms was found to take place predominantly with the ether oxygens of the same arm rather than the other arms' carbonyls. According to DFT calculations, the silver cation preferred to coordinate with one sulfur bridge and three carbonyl groups, whereas potassium cation favored interaction with the four carbonyl oxygens of the podand amide arms. Neither cation preferred the N-mode of coordination. For all obtained conformers, intramolecular hydrogen bonds disfavor complexation, increasing the preorganizational energy to be paid.

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